

PYROLYTIC OIL-PRODUCTIVITY INDEX METHOD FOR PREDICTING RESERVOIR ROCK AND OIL CHARACTERISTICS

Field of the Invention

This invention relates to the use of data derived from the pyrolytic oil-productivity index, or POPI, to further predict other characteristics of the oil-bearing reservoir rock and the characteristics of the oil in the reservoir.

Background of the Invention

A method for characterizing reservoir rock from the pyrolytic analysis of rock samples known as the Pyrolytic Oil-Productivity Index Method, or "POPI method", is disclosed in USP 5,866,814. The disclosure of USP 5,866,814 is incorporated herein in its entirety by reference.

In the practice of the POPI method, the quality of the reservoir rock at a given location and depth is characterized as (a) oil-producing; (b) marginally oil-producing; or (c) non-reservoir or tar occluded. These relative characterizations are based on a comparison of the value of $POPI_x$ for a given rock sample X with the value of $POPI_o$ that has been previously determined from either (1) oil-stained reservoir rock samples similar to the drilling target that are known to be of good reservoir quality; or (2) a sample of oil that is similar to the expected composition of the well's target zone. The principal advantage of the POPI method is its ability to provide data in real time based on cutting samples taken from the drill rig, so that on-the-fly changes can be made, e.g., in horizontal drilling directions, to keep the bit in oil-producing reservoir rock.

The POPI method can also be used to amass a body of comparative data for a given region or an oil field that can be used in planning further exploration and production.

The analytical procedures for determining the values for POPI are described in USP 5,866,814 (Jones and Tobey), and in view of the relationship of the present invention to the POPI method, the following summary is provided to facilitate an understanding of the terminology and significance of the data points.

1. Definitions

As used in this specification and claims, the following terms have the meanings indicated:

HC means hydrocarbons.

ln means natural logarithm.

LV is the weight in milligrams of HC released per gram of rock at the static temperature condition of 180°C (when the crucible is inserted into the pyrolytic chamber) prior to the temperature- programmed pyrolysis of the sample.

TD is the weight in milligrams of HC released per gram of rock at a temperature between 180°C and T_{\min} °C.

TC is the weight in mg of HC released per gram of rock at a temperature between T_{\min} °C and 600°C.

LV+TD+TC represents total HC vaporizing between 180°-600°C. A low total HC indicates rock of lower porosity or effective porosity. A low value can also indicate zones of water and/or gas.

POPI₀ is the value of the pyrolytic oil productivity index as calculated for a representative sample of crude oil of the type which is expected to be found in good quality reservoir rock in the region of the drilling and chosen as a standard.

T_{min}(°C) is the temperature at which HC volatilization is at a minimum between the temperature of maximum HC volatilization for TD and TC and is empirically determined for each sample. Alternatively, a temperature of 400°C can be used for samples where there is no discernable minimum between TD and TC. The latter sample types generally have very low total HC yields.

Phi is the average porosity of the rock.

Sxo is the saturation of drilling mud filtrate and represents the amount of HC displaced by the filtrate, and therefore, movable HC.

Phi*Sxo vs depth plot - the area below the curve represents the proportion of porosity which contains movable HC.

Phi vs depth plot - the area between the Phi curve and the Phi*Sxo curve represents immovable HC, or tar.

Gamma - the naturally occurring gamma rays that are given off by various lithologies while measuring directly in the well bore by the prior art petrophysical tools and are reported in standard API (American Petroleum Institute) units.

Caliper - the measured diameter of the well bore taken at the time of running petrophysical logs.

Density porosity - the porosity calculated by prior art methods from the petrophysical bulk density tools using an assumed fluid and grain density.

Neutron porosity - the porosity measured by prior art methods from petrophysical neutron tools.

Deep resistivity - the resistivity measured by deep invasion (long spacing between source and receiver), lateral log or induction petrophysical tools which is used as a measurement of undisturbed formation resistivity.

Medium resistivity - the resistivity measured by medium invasion (medium spacing between source and receiver), lateral log or induction petrophysical tools which is used as a measurement of resistivity of the formation that has been flushed by mud filtrate from the drilling fluid.

Shallow resistivity - the resistivity measured by shallow invasion (short spacing between source and receiver), lateral log or induction petrophysical analytic techniques which is used as a measurement of the resistivity of the mud filtrate from the mud cake that forms on the interior of the well bore during drilling operations.

Neutron-density cross-plot porosity (N-D Phi) - the porosity determined from a common prior art method which compensates for the effects of lithologic and fluid changes that lead to inaccuracies in employing either density or neutron porosity measurements by themselves.

Core plug permeability - the permeability measured by prior art methods from cylindrical rock samples that are cut from cores taken from the drilling process that is reported in units of millidarcys (md).

2. Pyrolysis Analytical Procedure

The analytical method used to quantitatively determine the presence of hydrocarbons in reservoir rock samples is known as open-system pyrolysis. In the practice of the POPI method of the invention the following expression is used to provide one or more data points:

$$\ln(LV+TD+TC) \times (TD \div TC) = POPI \quad (I)$$

In the above expression, the term " $\ln(LV+TD+TC)$ " means the natural logarithm of the value and the term "POPI" is used as shorthand for Pyrolytic Oil Productivity Index. The term POPI is also used more broadly hereinafter as a reference to the method of the invention.

In the POPI method for pyrolysis, a time and temperature-programmed instrument heats a small amount of ground rock sample from a starting temperature of 180°C (held for 3 minutes) to 600°C at a rate of increase in temperature of 25°C per minute. During the programmed heating, the hydrocarbons driven from the rock are recorded as a function of temperature. Fig. 1 shows a typical instrument output plot, which is known as a "pyrogram". A typical analysis results in three peaks. The first is composed of hydrocarbons that can be volatilized, desorbed, and detected at or below 180°C while the temperature is held constant for the first 3 minutes of the procedure. These are called light volatile hydrocarbons, or "light volatiles" (LVHC, or LV). The next phase of the pyrolytic analysis consists of a programmed temperature increase from 180°C to 600°C that usually results in two more distinct peaks. The first of these peaks occurs between 180°C and about 400°C, and corresponds to thermal desorption of solvent-extractable bitumen, or the light oil fraction. These are called thermally distilled hydrocarbons (TDHC, or TD). The second peak in this phase (third peak overall) occurs after about 400°C, generally after a minimum in pyrolytic yield is observed and extends typically to about 550°C.

The temperature corresponding to the minimum in pyrolytic yield between TD and TC is referred to as T_{MIN} . This peak is due to the pyrolysis (cracking) of heavier hydrocarbons, or asphaltenes. The materials that thermally crack are called thermally cracked hydrocarbons or "pyrolyzables" (TCHC, or TC).

5 As will be understood by those familiar with the art, many other types of data are employed in the characterization of reservoir rock and the oil in the reservoir for the purposes of modeling exploration and production. It is therefore an object of the invention to provide improved methods for determining the characteristics of reservoir rock and the oil in the reservoir based on the POPI method.

It is another object of the invention to provide an improved method for determining reservoir rock characteristics relating to water saturation and to API oil gravity that is less expensive, faster and of comparable accuracy to methods known in the prior art.

It is yet another object of the invention to provide an improved method for determining apparent water saturation values (AS_w) from preserved core samples and from core samples that have not been specially preserved, and also by a method that is not dependent on data obtained from petrophysical or electric log data.

Another object of the invention is to provide an improved method that will serve as a substitute for the Dean-Stark method and apparatus for estimating water saturation.

20 Yet another object of the invention is to provide an improved method of determining water saturation that is both qualitative and quantitative and which is superior to the Dean-Stark calculations when the reservoir contains inhomogeneities, light oil, and/or oil-water transition zones.

A further object of the invention is to provide an improved laboratory method that closely matches the water saturation S_w value as determined by calculation from electric log data employing the Archie equation.

A further object of the invention is to provide a method for assessing changes in the saturation and cementation exponents that are required in utilizing the Archie equation.

Summary of the Invention

The above objects and other advantages are achieved by the improvements of the invention in the pyrolytic oil-production index method, or POPI method. In accordance with one aspect of the invention, the numerical values obtained by the application of the prior art POPI method are standardized or normalized.

In another aspect of the invention, the POPI method and associated data are employed in combination with other empirically determined information to provide values of (1) the API gravity for the reservoir oil; (2) the Apparent Water Saturation (AS_w) of the reservoir rock; and (3) the cementation and saturation exponents that are used in the Archie equation for calculating the water saturation in the oil-reservoir rock.

The improved method of the invention results in the standardization of the numerical values derived by the POPI method. Applying the normalization or standardization process to the POPI method results in the conversion of the numerical value of $POPI_0$ for good oil-producing reservoir rock to a standard value, e.g., 100, which is denominated $POPI_{NORM}$; a sample considered to be non-reservoir rock has a numerical value less than 50 (i.e., less than one-half the original value of $POPI_0$); and sample values from $1/2 POPI_0$ to $POPI_0$ that are

considered to be marginally productive reservoir rock have corresponding numerical values, i.e., between 50 and 100. This normalization or standardization of $POPI_0$ values has several advantages over the method of the prior art, including that of providing a basis for making direct comparisons between and among the indices for different wells and/or regions.

5 The Pyrolytic Oil-Productivity Index (POPI) method of the prior art is improved in accordance with the invention to utilize a normalized scale, referred to as $POPI_{NORM}$, that is based on a standardized value that indicates good to excellent oil-productivity for the reservoir rock. In a preferred embodiment, the standardized or normalized value is 100. As will be apparent to one of ordinary skill in the art, another value, e.g., 1000, can be used for the purpose of the invention. However, a value of 100 provides a convenient normalization value for the use and analysis of the data. The method comprises the steps of calculating a normalization factor, F_{NORM} , that is applied to the POPI values that were calculated in accordance with the method of the prior art. The improved method for determining cut-off values for POPI renders POPI data easier to compare from well to well and from field to field.

10 The invention also comprehends three related improved methods that enhance the range of information available for the characterization of oil reservoirs. The first is the method for predicting the API gravity of an oil in a reservoir by direct calculation from a series of POPI measurements on non-preserved cores or cuttings.

15 The second method of the invention is directed to the calculation of the in-reservoir water saturation (S_w) value from pyrolysis of reservoir rock samples that are derived from either non-preserved cores or fresh rock cuttings recovered at the drill site. The practice of the method is cost-effective, rapid and is not labor intensive, allowing a large number of samples to be

processed for an individual well. The end result is an Apparent Water Saturation (AS_w) curve produced by direct measurements that can be compared to water saturation (S_w) as calculated by the Archie Equation from indirect down-hole electric log data.

The third improved method is an extension of the determination of the Apparent Water Saturation (AS_w). Using the AS_w curve, inferred values for the cementation exponent (m) and the saturation exponent (n) are calculated from the electric log data that satisfy the Archie Equation, as well as the pyrolytic data (AS_w). The magnitude of the variation of the m and n values compares favorably to the variations present in direct petrophysical measurements on core samples. These values are extremely useful in developing accurate reservoir models, as well as for estimating reservoir reserves. These improved methods have utility as calibration tools for developing additional input data used in reservoir modeling.

Brief Description of the Figures

The invention and its preferred embodiments will be further described with reference to the attached figures in which:

FIG. 1 is a typical prior art pyrogram from an open-system temperature-programmed pyrolysis of an oil sample, indicating the areas associated with the data used to calculate the POPI values in accordance with formula (1);

FIG. 2 is a plot of POPI versus Total Hydrocarbons (LV+TD+TC) showing prior art linear interpolations to determine $POPI_0$ for two different oils;

FIG. 3 is a series of plots of POPI versus Total Hydrocarbons (LV+TD+TC) for a suite of oils with substantially different pyrolytic character;

FIG. 4 is a plot of depth versus predicted API gravity based on pyrolytic data ratios for individual core samples;

FIG. 5 is a plot of the POPI Pre-Logarithmic Coefficient versus API Gravity for the oils of Fig. 3;

5 FIG. 6 is a plot of pyrolytic yield versus API gravity;

FIG. 7 is a plot of POPI versus Total Hydrocarbons (LV+TD+TC) for a well-behaved data set of reservoir rock samples;

FIG. 8 is an example of curve-fitting POPI versus Total Hydrocarbons to assess PPLC and API gravity;

FIG. 9 is a plot of API Gravity computed from PPLC of oils and reservoir rock samples versus the actual API Gravity values determined from the oil samples or from the produced oils from the respective wells with reservoir rock samples;

FIG. 10 is a plot of API Gravity from PPLC on reservoir rock samples versus API Gravity measurements of the corresponding oils;

FIG. 11 is a comparative graphic plot of POPI and Core Plug Permeability versus Depth for a well exhibiting a well-defined oil-water contact;

FIG. 12 is a graphic plot of POPI versus Total Hydrocarbons (LV+TD+TC) for a well with a relatively low correlation of the PPLC;

FIG. 13 is a graphic plot of POPI versus Total Hydrocarbons (LV+TD+TC) with iso-
20 AS_w lines separating fields of similar AS_w values;

FIG. 14 is a graphic plot of Depth versus Apparent Water Saturation (AS_w);

FIG. 15 is a comparative graphic plot of depth profiles on a composite log for Apparent Water Saturations (AS_w) from pyrolytic data, and for petrophysical log and derived data obtained by prior art methods;

FIG. 16 is a comparative graphic plot of depth profiles presented on a composite well log for Apparent Water Saturation (AS_w) as calculated from pyrolytic data, and for petrophysical log and derived data obtained by prior art methods; and

FIG. 17 is a comparative graphic plot of depth profiles on a composite well log that includes Apparent Water Saturation (AS_w) as calculated from pyrolytic data, recalculated water saturation using variable cementation (m) and saturation (n) exponent values as annotated, and petrophysical log and derived data obtained by prior art methods.

Detailed Description of the Invention

The various aspects and embodiments of the invention are described with reference to the attached drawings sheets in which the figures are comprised of graphs or plots of data or data sets that are based on empirical information for actual wells. The information is believed to be representative for the purposes of describing the improved methods of the invention. As will be understood by one of ordinary skill in the art of developing and interpreting such geophysical data for the purposes of characterizing reservoir rock and its petroleum contents, marked variations do occur between regions, and even within regions due to geological anomalies. In any event, the detailed description of the invention, when read in conjunction with the drawing figures, provides a teaching sufficient to put one of ordinary skill in possession of the invention.

Normalization of POPI Values

In order to provide a standard set of values for the POPI obtained from numerous well sites in a region, or to enable a ready comparison of data from several geophysical and/or geographical regions, a normalization function is applied to the POPI values.

By way of example, and for the purpose of describing the preferred embodiment of the invention, the normalized value for $POPI_0$ is designed to have a value of 100. It will be understood that the value of $POPI_0$ for any given set of pyrolytic data is determined in accordance with the method described in USP 5,866,814, and above.

The practice of the improved method of the invention comprises the steps of:

- (a) determining the value of $POPI_0$ in accordance with the prior art equation

$$POPI_0 = \ln(LV + TD + TC) \times (TD \div TC); \quad (1)$$

- (b) calculating the value of the normalization factor F_{NORM} in accordance with the following equation (2):

$$F_{NORM} = \frac{100}{POPI_0}; \quad (2)$$

- (c) normalizing the value of $POPI_X$ derived from a given rock sample "X" in accordance with the following equation (3A):

$$POPI_{NORM(X)} = F_{NORM} \times POPI_X; \text{ and} \quad (3A)$$

- (d) recording the value of $POPI_{NORM(X)}$.

This normalization process is repeated for values obtained for rock sample "Y" and for the POPI data obtained for all samples in the desired set of samples. Thereafter, the data can be manipulated as desired, and printed in graphic or tabular form. From the above, it will be

understood that negative POPI values remain negative; however, they become larger negative numbers, and they still indicate a hydrocarbon saturation that is too low to be within an oil column, thus being either wet, in a gas zone, or in very tight rock. The advantage of this new analysis regimen is to make POPI more amenable to direct comparison between wells with substantially different oil characteristics.

Calculation of API Gravity from POPI Data

As noted above, $POPI_0$ is the Pyrolytic Oil-Productivity Index value that is expected for a rock sample with good reservoir quality given that it is sufficiently high in the oil column to be free from the oil-water transition zone, and that the characteristics of the produced oil are consistent with those that were anticipated. Previously, two principal methods were used to determine the value of $POPI_0$. One method of determining the value of $POPI_0$ was to analyze a series of samples from a reservoir, determine the POPI value for each of the samples, produce a POPI versus depth plot for the set of samples and then compare the POPI values to reservoir quality as determined by conventional electric logs. In doing this, those areas with good reservoir quality usually have a range of POPI values, the minimum of which can be used to separate good quality reservoir rock (i.e., a higher POPI value) from the lower quality reservoir rock (i.e., a lower POPI value).

The other method used to determine $POPI_0$ was through an analysis of oil that is similar to the oil actually produced, or that is expected to be produced, in the region from which the rock or core samples to be tested were obtained. The latter procedure is outlined below:

- 1) To 1 cc of the oil sample, add 9 cc of a suitable solvent, such as methylene chloride, dimethyl sulfide or other suitable solvent that will completely dissolve the oil sample and that is readily evaporated at or below 60°C.
- 2) Prepare 9 steel crucibles with approximately 100 mg of clean silica gel.
- 3) Apply to the silica gel, e.g., by a syringe, three samples each of the solution of the oil in solvent quantities of 10, 20 and 30 microliters.
- 4) Dry the samples at 60°C in the crucibles in a vacuum oven for 4 hours.
- 5) Subject the samples to pyrolytic analysis, using 100 milligrams as the required input sample size for the instrument to provide data corresponding to LV, TD, and TC.
- 6) Utilize standard spreadsheet and graphics software to input the data and prepare a chart or plot (such as that of Fig. 2) with the y-parameter being the POPI value and the x-parameter being the sum of total hydrocarbons (LV+TD+TC).
- 7) Select the range for the value of $POPI_0$ from the chart where the value of total hydrocarbons is between 4-6 milligrams per gram of sample.

According to the disclosure of USP 5,866,814, column 7, lines 30-39, it was understood that a total hydrocarbon value in the range of from 4-6 milligrams was fairly typical for residual staining after sample preparation from oils that are less than 42° API gravity. It was also taught that lighter oils having higher API gravity values could require the use of lower values for total hydrocarbons, since the residual hydrocarbon staining could be significantly lower due to evaporation of the light components and lower amounts of the medium and heavy components. Therefore, it was stated that evaluation of good quality and productive reservoir rock was the

preferred means for determining the value of POPI for those reservoirs yielding oil having an API gravity greater than 42°.

A more accurate understanding of the relation between the change in the POPI value with changes in oil characteristics has now been determined as a result of the analysis of a large number of crude oil and rock samples. Fig. 3 is a plot of POPI values versus total hydrocarbons (LV+TD+TC) for a set of oil samples that were analyzed by the procedure of steps (1) through (7) as set forth above. In this sample set, the samples ranged in volume from 10, 20 and 30 micro-liters and included some samples of up to 80 micro-liters. As will be seen from Fig. 3, the striking characteristic of the plot of the test data is that the best-fit for the variation of POPI is not linear, as previously suggested by Fig. 2 of the prior art, but rather, the trend of the data is logarithmic. This is apparently attributable to the fact that the POPI calculation includes the natural logarithm of the total hydrocarbons in its equation.

Various other methods of estimating API gravity values from pyrolytic data have been developed. These methods have a common feature in that they produce a separate API gravity determination for each sample analyzed. Moreover, when considering a well profile, these predicted API gravities show considerable variation, especially when an oil-water transition zone is encountered as shown for the example in Fig. 4. However, during production of a well, a single API gravity is generally representative of the produced oil.

Based on this practical determination, the relationship is established for each of these oil samples by the following equation (4):

$$\text{POPI} = \text{PPLC} \times \ln(\text{LV} + \text{TD} + \text{TC}) + b \quad (4)$$

where PPLC is the POPI Pre-Logarithmic Coefficient and is a constant for a given type of oil;

\ln is the natural logarithm;

$(LV+TD+TC)$ is the total quantity of hydrocarbons in a sample; and

b is an empirically determined constant.

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It has been found empirically that the constant b is typically less than about 0.1, and since variations in POPI of this magnitude are not significant, the value of b can be disregarded. Thus, for the purpose of the practice of the invention, the above equation (2) is simplified to equation (5):

$$POPI_{oil} = PPLC \times \ln(LV+TD+TC) \quad (5)$$

where $POPI_{oil}$ is the value of POPI obtained by varying concentrations of oil on either a silica gel substrate or on reservoir rock samples; and the other terms are as defined above.

The values of $POPI_{oil}$ at various concentrations are plotted to provide a trend line, the shape or curve of which reflects the characteristics of the oil. From equations (4) and (5) above, it will be understood that it is the PPLC that determines the shape of the curve resulting from the plot of POPI versus total hydrocarbons. In accordance with another aspect of the invention, the value of the PPLC, and hence the shape of the curve, is directly related to the API gravity of the reservoir oil. Fig. 5 is a plot of the PPLC versus the API gravity of the various oil samples. As can be seen, the plot of PPLC versus API gravity data exhibits an excellent exponential fit, with a high correlation coefficient $r=0.967$. As a result, API gravity alone can be used to calculate the value of the PPLC; conversely, the PPLC can be used to calculate API gravity. The validity of this relationship was established by comparisons of empirical data from

a geographically large oil production region. As will be understood by one of ordinary skill in the art, other basins or regions may require the determination of their own specific values. However, the principles and underlying behavior of the equation are the same. Therefore, steps to develop alternative relationships for other basins result in relatively minor overall differences.

Thus, for a given data set, the following equation (6) can be used for determining the PPLC:

$$PPLC = PEC \times e^{(c \times API)} \quad (6)$$

where PEC is the pre-exponential coefficient (determined empirically from the data to be about 0.151);

e is the base value for the natural logarithm (an irrational number with a decimal approximation of 2.718281);

c is a constant (determined empirically from actual field data to be about 0.0976); and

API is the numerical value of the API gravity.

Substituting the numerical values in (6) above:

$$PPLC = 0.151 \times e^{(0.0976 API)} \quad (6A)$$

This equation can be solved for API gravity in terms of PPLC as:

$$API = [\ln(PPLC/PEC)]/c, \text{ or} \quad (6B)$$

$$API = [\ln(PPLC/0.151)]/0.0976 \quad (6C)$$

From equations 6 and 6A-6C above, a variety of relevant information can be determined.

First, $POPI_o$, the cut-off value for POPI that is consistent with good reservoir quality, can be calculated from the API gravity alone using a simplified version of equation (6). Since the constant in equation (4) is negligible, then:

$$POPI_o = PPLC \times \ln(HC_{MIN}) \quad (7)$$

where HC_{MIN} is the minimum quantity of residual hydrocarbon staining for good quality reservoir rock located above an oil-water transition zone.

As previously noted, based on empirical data, this value is between 4-6 milligrams of total pyrolytic yield (LV+TD+TC) gram of rock. Results of oil analyses have also yielded a method for estimating HC_{MIN} from the actual anticipated API gravity of a sample. Fig. 6 is a cross-plot of total pyrolytic yield (LV+TD+TC) per 10 microliters of oil sample versus API gravity. The data show that with increasing API gravity, the expected yield for the same quantity of original hydrocarbons decreases. This is due to evaporation of the lighter components, especially LV, in the higher gravity samples. The POPI value derived from pyrolytic data from a reservoir containing 31° API gravity oil on this plot yields a value of 5 milligrams total HC/microliter of oil. Therefore, in good quality reservoir rock, after accounting for the effects of flushing the rock with mud filtrate and the sample preparation, only staining, representative of 10 microliters per gram of original in-reservoir oil remains. Of the remaining residual hydrocarbons, the total yield varies with the API gravity in accordance with the following:

$$HC_{MIN} = 577 \times API^{-1.38} \quad (8)$$

Using this relationship, HC_{MIN} is substituted in equations (5) or (7) to solve for the POPI cut-off value for good quality reservoir rock as follows:

$$POPI_o = PPLC \times \ln(577 \times API^{-1.38}) \quad (9)$$

PPLC, and hence, $POPI_o$, can then be determined either through data analysis on a set of samples, or by solving equation (6) using API gravity. Fig. 7 is a typical cross plot of POPI values versus total hydrocarbon yield (LV+TD+TC) that exhibits a well-behaved set of data

from reservoir rock samples. In this case, the solid curve is the logarithmic trend line generated from the data set and can be expressed by the equation:

$$POPI = 7.48 \ln (\text{Total Hydrocarbons}) - 3.2 (\text{correlation coefficient } r = 0.94).$$

The dashed curve is a hypothetical line that represents an oil with the same PPLC as the rock data (approximately 7.5), and an insignificant constant b. This curve is representative of the curve that is generated by the actual oil sample, that is $POPI = POPI_{oil}$, where $POPI_{oil}$ is the POPI value that the oil would have given at any total hydrocarbon yield. Thus, the PPLC as determined by plotting these data can now be used in equation (7) to calculate $POPI_o$, and if the API gravity is unknown, then it can also be determined through equation (6) and then used for estimating HC_{MIN} in equation (8).

As shown above, API gravity can also be estimated through the analysis of POPI data. For a set of data generated from either an oil sample (using the above method for determining $POPI_o$ from oil samples, e.g., as in Fig. 3) or from core or drill cutting samples, a plot of POPI versus total hydrocarbons (LV+TC+TC) is generated, as in Fig. 7. From this plot, the POPI Pre-Logarithmic Coefficient (PPLC) is obtained by fitting the data to a logarithmic curve. As shown in Fig. 5, the PPLC has an excellent exponential fit when plotted against API gravity, and expressed by equation (3), (correlation coefficient $r = 0.98$).

For reasons that will be described later, POPI data for reservoir rock samples often do not produce a clear trend with most data points falling along a trend line in accordance with equation (5), as, for example, Fig. 8. In such cases, an iterative approach can be employed in accordance with the method of the invention and a hypothetical line for $POPI_{oil}$ can be constructed utilizing various values for the PPLC factor until a satisfactory curve fit is obtained,

with the highest POPI values recorded for given total hydrocarbon quantities. The POPI data in this case can be viewed as fitting in the envelope formed by the X-axis and the line described by the equation:

$$POPI_{oil} = PPLC \times \ln(LV + TD + TC).$$

Fig. 9 is a cross plot of API gravity as determined from the PPLC versus measured API gravity for oils and the produced oils from wells corresponding to the reservoir rock samples analyzed. Of particular significance in the method of the invention is the fact that the slope is very close to 1(0.94), the intercept is small (1.7), and the correlation coefficient is very high ($r=0.97$). This plot demonstrates that the method of the invention can be employed over a wide range of API gravities and that the difference between the API gravity predicted from PPLC is generally within 2-3 API gravity units, or less. Fig. 10 is the same plot as Fig. 9, but employs only the rock data. For this set of data, the correlation is somewhat lower (correlation coefficient $r=0.87$) due to the fact that the sample set ranges only from 27-42° API gravity. However, the fit is still good, and the difference between the API gravity and that predicted from the PPLC is generally within 2-3° API, or less.

Determination of Apparent Water Saturation from POPI Data

From an analysis of POPI field data, it was observed that POPI values decrease markedly in oil-water transition zones and that POPI values generally become negative at the base of the transition zone. See, for example, Fig. 11. This is due to two factors: 1) total hydrocarbon saturation decreases with increasing water saturation resulting in decreasing pyrolytic yield; and 2) with increasing water saturation there is a decrease in the proportion of the lighter

components (LV and TD) as compared to the asphaltene (thermally crackable, TC) components that comprise the oil.

The increase in heavier (TC) components relative to the lighter components (LV+TD) associated with increasing water saturation is believed to be the result of differential absorption effects. In an oil reservoir, the system begins as rock matrix with water-filled pores. As the reservoir fills with oil, a given portion of the reservoir will experience either sufficient capillary pressure to replace the water with hydrocarbons to a point where the water saturation is at an irreducible level (S_{wirr}), or the capillary pressure will be sufficient to displace only a portion of the water in the pores ($S_w > S_{wirr}$). It has been found that the residual staining on the rock matrix resembles the original oil ($POPI = POPI_{oil}$) only when the reservoir has attained (or nearly attained) a condition of irreducible water saturation and that the irreducible water saturation is generally low (e.g., <20%). In this case, the relative absorption A of the components representative of the LV, TD and TC pyrolytic products is similar enough so that the staining matches the oil characteristics very closely, that is $A_{LV} \approx A_{TD} \approx A_{TC}$. However, as the final hydrocarbon saturation for a particular portion of the reservoir results in progressively greater water saturation (S_w), the relative absorption of the heavy components (TC) is favored over the lighter components (LV+TD) such that the absorption of LV is less than or approximately equal to the absorption of TD, which is much less than the absorption of TC. This can be expressed mathematically as: $A_{LV} <, \text{ or } \approx A_{TD} < < A_{TC}$.

The method of the invention for determining the Apparent Water Saturation (AS_w) from pyrolytic data is based upon the recognition of: (1) the above understanding of differential absorption effects, and (2) the generally decreasing hydrocarbon yield associated with increasing

water saturation. Two endpoints can be defined that correspond to these conditions: (1) water saturation is at an irreducible level (e.g., S_w is between 0.05 to 0.1 on a pore volume-to-pore volume basis), and the corresponding residual hydrocarbon staining closely resembles the reservoir oil, resulting in a condition where, for a series of reservoir rock samples analyzed, $POPI = POPI_{oil}$; or (2) water saturation is very high ($S_w = 1.00$), residual staining does not resemble the reservoir oil ($A_{TC} \gg A_{TD}$, or $\approx A_{LV}$), and total hydrocarbon yield is very low ($(LV + TD + TC) \approx$ or $< 1.0 \text{ mgHC/gRock}$), resulting in a POPI value that is near or below zero.

Thus, on a plot of POPI versus total hydrocarbons ($LV + TD + TC$), these two endpoints can be clearly identified. Fig. 7 is an example of a POPI versus total hydrocarbon plot for a well-behaved data set (i.e., the logarithmic fit of the data set for the rock samples results in a high correlation coefficient, $r = 0.94$). In this example, the solid line is the logarithmic fit of the data and the dashed line is the hypothetical line assumed to match the oil characteristics, and as such, is defined as $POPI = POPI_{oil}$. Along the dashed line corresponding to $POPI = POPI_{oil}$, it is assumed that the rock is completely saturated with oil ($S_o = 1.0$, $S_w = 0.0$) and that any data points falling on this line, or above it, represent rock samples whose pore spaces are fully saturated by oil. Since irreducible water saturations cannot be less than about 0.05 in practice, the line $POPI = POPI_{oil}$ is set to $(1 - S_{wirr})$ and any calculated Apparent Oil Saturation (AS_o) that exceeds 0.95 is set equal to 0.95. The other line on the plot represents the condition where $POPI = 0$ (the x-axis) and this corresponds to full water saturations ($S_o = 0$, $S_w = 1.0$). With these two endpoints, the calculation of AS_o and AS_w for any given data point is a simple linear interpolation between the $POPI_{oil}$ value corresponding to the particular total hydrocarbon yield

of the sample and the x-axis. Thus, for a given sample "a" with pyrolytic data corresponding to LV_a , TD_a , and TC_a :

$$POPI_a = TD_a \div TC_a \times \ln(LV_a + TD_a + TC_a), \quad (1a)$$

$$POPI_{oil,a} = PPLC_{API} \times \ln(LV_a + TD_a + TC_a)$$

$$AS_o = (1 - S_{wirr}) \times POPI_a \div POPI_{oil,a}, \quad \text{and (10)}$$

$$AS_{w,a} = 1 - AS_{o,a}. \quad (11)$$

Figure 12 is an example employing the method to a data set of samples that is not very well-behaved in that the logarithmic fit (solid line) of data results in a low correlation coefficient ($r=0.75$) and the PPLC is high (9.69) as compared to that predicted from API gravity (7.6), resulting in an API gravity prediction of 42.7° as compared to the actual value of 40.2° for the oil that was produced from the well during testing. For the purpose of calculating the AS_w for this well, use of the PPLC value representative of the actual produced oil (dashed line, Fig. 12) is preferred.

The interpretation of the data can be portrayed graphically, see Fig. 13, by constructing a series of iso- AS_w lines that divide the plot into fields of similar AS_w . The interpretation of AS_w for a well is most often portrayed in a Depth versus AS_w plot, as illustrated by Fig. 14. As will be understood from the Depth versus AS_w plots, the AS_w can vary greatly over short depth intervals. AS_w data are most often compared to S_w as determined by the Archie equation. Because of this fact, smoothing the data by using an arithmetic mean applied over a 3-5 ft. interval is a preferred method of simulating the resolution of electric logs with AS_w data, thereby simplifying data comparisons as, for example, the dashed line in Fig. 14.

Another laboratory method to determine water saturation is the "Dean-Stark Method for Oil and Water Saturation Measurement." The application of AS_w has several benefits over the Dean-Stark method, including: (1) the turn-around time is much more rapid than the Dean-Stark method; (2) organic solvents are not used during the pyrolytic technique, resulting in reduced costs and environmental and health benefits; (3) the AS_w method does not require preserved cores, which are much more costly to acquire and later handle to obtain quantitative results; (4) the AS_w method can utilize drill cutting samples; and (5) the AS_w method is accurate over a wider range of oil types, i.e., from API 17° to API 42°.

Figure 15 is a composite well log that allows the comparison of saturation data from the Dean-Stark method, the AS_w method and S_w from the Archie Equation, to other electric log data. The composite log in Fig. 15 consists of seven log "tracks" with the following information: Track 1 contains the spontaneous potential (SP), gamma ray (GR) and caliper (CAL); Track 2 contains a graphical representation of lithofacies; Track 3 contains lithofacies description in text form; Track 4 contains density porosity (DPLE) and neutron porosity (NPHI); Track 5 contains the deep investigation (ILD), medium investigation (ILM), and shallow investigation (MSFL) resistivity logs; Track 6 contains apparent water saturation (AS_w), and water saturation (S_w) calculated by the Archie Equation ($RDD.S_w$); and Track 7 contains the saturation of oil and water from Dean-Stark analyses that are identified as DEAN-STARK.SO and DEAN-STARK.SW, respectively. In Fig. 15, the apparent water saturation (AS_w) and the Archie Equation water saturation (S_w , $RDD.S_w$) match very closely. Here, the AS_w data presented are the same as in Fig. 14 and have been smoothed by applying an arithmetic mean over a 3 ft. sample rate. This demonstrates that the AS_w data obtained by the method of the invention are

quantitative and comparable to other industry standards for determining water saturation. The Dean-Stark data in comparison, are difficult to interpret. The oil saturation (DEANSTARK.SO) reaches the highest levels well below the actual hydrocarbon column. Also, the water saturation (DEAN-STARK.S_w) exhibits only a slight increase, corresponding to the very pronounced oil-water transition zone from 5050 to 5070 ft. The unreliability of the Dean-Stark data in this case is due to not having preserved core samples and the high proportion of light oil in the reservoir (API gravity ~ 40°). Thus, the method of the invention for estimating the AS_w for the data set is more reliable than the Dean-Stark method.

Calibration of Cementation (m) and Saturation (n) Exponents for Archie Calculations from Electric Logs

The most common method utilized in the petroleum industry to determine the saturation of the reservoir rock by water (and hence, by difference, the saturation of hydrocarbons) is the application of the Archie Equation (Archie, 1942; Chen and Fang, 1986) to resistivity and porosity electric log data.

The basic Archie Equation, as it is applied in the method of invention, can be expressed as (12):

$$S_w = (1/\phi^m \times R_w/R_t)^{1/n} \quad (12)$$

where S_w is the water saturation,

φ is the porosity from electric logs,

m is the cementation exponent as determined from lab tests,

R_w is the formation water resistivity as determined from electric logs or as determined by laboratory measurements of formation water samples,

R_t is the true resistivity of the formation as measured by deep investigation resistivity tools, and

n is the saturation exponent as determined by lab tests.

5 There are a variety of well-known laboratory techniques for the determination of the value of the exponents m and n . However, these techniques are time-consuming and require extensive man-power. Therefore, it has been a common practice in the prior art to determine these parameters empirically by performing iterative applications of the Archie Equation while varying the values of m and n such that reservoirs that are oil-filled ($S_w = S_{wirr}$) and water-filled ($S_w = 1.0$) yield acceptable water saturation values. Having determined acceptable values for m and n , these values are then applied over the entire reservoir interval, making the assumption that the parameters are uniform within the reservoir. This assumption can be reasonable in relatively consistent lithofacies. However, if substantial variations exist in reservoir properties, then significant errors can occur in estimating water saturation, and, therefore, hydrocarbon reserves attributable to a particular well. These errors can have a substantial impact on reservoir management issues and overall project economics.

20 The method of the invention for estimating the AS_w also yields another method for calibrating the values of m and n for the purpose of improving the accuracy of the Archie Equation calculations. In one embodiment, the method of the invention comprehends performing iterative applications of the Archie Equation while varying the value of m and n such that the calculated S_w as determined by the Archie Equation closely matches that determined by the AS_w method. An example of employing this technique is illustrated by the following:

Two-hundred-thirty-five core samples taken from a single well were analyzed by pyrolysis using the methods described in USP 5,866,814 and summarized above. The sampling interval was from 4918.8 ft. to 5306.7 ft., i.e., about 388 ft. Fig. 16 is a composite well log consisting of basic electric log data, lithofacies descriptions, and in Track-6, apparent water saturation (AS_w , SMOOTH. AS_w) as calculated from pyrolytic data, water saturation (S_w) as calculated by the Archie Equation, (RDD. S_w) from electric log data, and individual values for irreducible water saturation (S_{wirr}) as determined by laboratory analyses. In general, the Archie calculated and pyrolytic S_w values closely agree between 4920 ft. and 4973 ft. Below 4973 ft., however, the AS_w data have a consistently higher Apparent Water Saturation (AS_w) than that calculated by the Archie Equation from electric log data (RDD. S_w). The cause for the inconsistency is apparently due to a lessening of reservoir quality, which would produce either a higher irreducible water saturation (S_{wirr}), or a considerably different capillary pressure curve with a correspondingly longer transition zone. The determination of irreducible water saturation on core plug samples by the laboratory analyses, in this case, assists in identifying the cause of these differences. Below is a table of the values for S_{wirr} , cementation exponent (m), and saturation exponent (n) values for four (4) core samples as determined in the lab.

<u>Core Depth</u>	<u>S_{wirr}</u>	<u>m</u>	<u>n</u>
4945.6	0.15	2.20	1.89
4946.1	0.54	2.18	2.99
4961.5	0.12	2.10	1.92
4986.6	0.45	1.94	1.8

As shown by the above data and the plot in Fig. 16, the S_{wirr} can vary widely over a very short interval. Moreover, the range of variation is equivalent to the magnitude of the variation of the AS_w values where the samples are located sufficiently above the oil-water transition zone such that $S_w = S_{wirr}$. In Fig. 16, the samples down to 4986.6 ft. correspond to the AS_w data, indicating that the relative increases of AS_w over Archie S_w are the result of increasing irreducible water saturation values. Below 4986 ft., the fact that the AS_w values are generally above the S_w values indicates that either these samples are from an oil-water transition zone, or there is an increase in the S_{wirr} value. Another significant observation regarding the differences in the AS_w and Archie S_w data is the approximately 25 ft. of significant hydrocarbon saturation below the base of the hydrocarbon column for the Archie S_w curve (RDD. S_w , 5040 to 5065 ft.). This indicates the presence of better than average reservoir properties in this zone than would be inferred from the application of uniform m and n values.

As a means of assessing the variation in reservoir quality and its effect on the cementation and saturation exponents, the S_w determined from electric logs was recalculated using variable cementation and saturation exponent values to solve the Archie Equation to produce results or values that closely match the AS_w data. The recalculated S_w values are shown in Fig. 17 (Track-6, RDD. S_w T). The values for the cementation exponent (m) and the saturation exponent (n) that were used for the various portions of the curve are annotated at the right hand side of the figure.

As can be seen from Fig. 17, reservoir sections between 4920 ft. and 4975 ft., between 5025 and 5045 ft., and below 5080 ft. have S_w and AS_w values that are fairly close. Therefore, m and n have been left at the uniform value of 2.0 that has been applied in this reservoir. Over

the rest of the reservoir, several intervals of differing m and n values ranging from 1.7 to 2.8 are employed to shift the recalculated Archie curve ($RDD.S_wT$) to provide a more consistent match with the AS_w values. Adjustments required in order to match S_w as calculated from data obtained by electric logs with the AS_w values (m and $n > 2$) suggest that poorer reservoir quality is present in zones with AS_w values substantially higher than the corresponding S_w values. Likewise, where AS_w is less than S_w , then the reservoir quality is predicted to be somewhat better than the average.

Importantly, the range of variation in the values of the m and n exponent values required to match AS_w data to $RDD.S_w$ data is comparable to the values determined from direct petrophysical analysis of core samples. This fact demonstrates that the inferred m and n values obtained by matching AS_w and S_w curves are meaningful, and that the method of the invention provides an accurate and effective improvement for calibrating these important input parameters for reservoir characterization and modeling.